24.0 Chromium Catalyst Users

24.1 Industry Profile

Chromium-containing catalysts are used to induce polymerization, to speed hydrogenation and dehydrogenation and are used in a reducing environment for gas production. Hexavalent chromium (chromium VI) containing catalysts are used in processes such as the production of plastics and polymers, in chemical synthesis, and gas production. In some processes, trivalent chromium (chromium III) catalysts are activated by heat and converted by oxidation to the hexavalent form.

Chromium catalysts remain stable during handling (Centaur, 1981). They are usually sold in powder form or in the form of specific shapes such as small pellets and are packaged in bags or drums. Pelletizing reduces the amount of dust generated during packaging and handling (Centaur, 1981). When catalysts are used, they are loaded into enclosed reaction vessels and, except for the Phillips polyolefins process described later, provide several years of service. During chemical processing operations, the hexavalent chromium containing catalyst typically remains within a totally enclosed catalyst-reaction vessel. At the end of its service life, a catalyst is removed from the vessel, usually by specialized catalyst service companies. Because specialized equipment, and employees with special training and equipment (such as for confined space entry) are required to load and unload catalysts, the vast majority of catalysts (over 90 percent) are handled by a catalyst service company (personal communication, Steve Brennom, Ken Waterhouse, 2003).

The facilities that use or handle hexavalent chromium containing catalysts are classified in Standard Industrial Classification (SIC) codes 28 and 7699 (Chemicals and Allied Products and Repair Shops and Related Services, not elsewhere classified, respectively). Although catalysts are used in the petroleum industry, there is only limited use of chromium-based catalysts in this industry, and these catalysts contain only trivalent chromium. Hexavalent chromium containing catalysts are not used in the petroleum industry (personal communication, Mike Lobue, Tom Sterling, and Dennis Leonard, 2003).

The applicable North American Industry Classification System (NAICS) codes for industries that use hexavalent chromium containing catalysts are shown below:

NAICS Code	Industry Title
325110	Petrochemical Manufacturing, including styrene
325120	Industrial Gas Manufacturing, including hydrogen and ammonia gas
325211	Plastics Materials, Synthetic Resins, and Nonvulcanizable Elastomers, including polyethylene
325199	Industrial Inorganic Chemicals, Not Otherwise Classified, including butadiene and methanol
561790	Other Services to Buildings and Dwellings, including catalyst-handling services

Hexavalent chromium-containing catalysts are handled in establishments that produce styrene, hydrogen and ammonia gas, polyethylene, butadiene, and by catalyst-handling service companies, which represent a small fraction of the total number of establishments within their respective NAICS Codes. Therefore, the Stanford Research Institute's Directory of Chemical Producers was used to obtain a more accurate number of establishments and firms that manufacture these products (SRI, 2003). Based on information obtained from a representative in the polyethylene production industry, approximately 40 percent of polyethylene is manufactured using hexavalent chromium containing catalysts, 40 percent of the total number of polyethylene production plants were used for this estimate. For NAICS 561790, the number of establishments, employees, and firms that provide catalyst-handling services was obtained through direct contact with a representative number of firms in the catalyst-handling service industry (personal communication, Steve Brennom, Andrew Clark, Paul Caskey, 2003).

Data on the number of affected establishments, employees, and firms for the hexavalent chromium catalyst users industry are presented in Table 24-1.

Table 24-1. Employment Data for Production of Styrene, Hydrogen Gas, Ammonia Gas, Polyethylene, Butadiene, Methanol and Catalyst Handling Services [a]

NAICS Code	Establishments[b]	Employees [c]	Firms[b]
325110	8	64	8
325120	123	984	70
325211	20	160 [d]	10
325199	12	96	8
561790 (Large) [e]	21	640	6
561790 (Small) [e]	4	60	4
Total	188	2,004	106

[a] All establishments and firms are classified as large employers, except small employers in NAICS 561790, as indicated.

[b] The number of establishments and firms in all NAICS Codes except 561790 were determined from company listings in the SRI Directory of Chemical Producers, 2003.

[c] The number of employees who are potentially exposed to hexavalent chromium was estimated to be 8 process operators per establishment, except NAICS 561790, including the catalyst service industry. The basis of this estimate is, according to the Meridian site visit described in Subsection 24.2, two process operators per shift handle hexavalent chromium-containing catalyst during addition to the process at Phillips polyolefins plants. Since these establishments operate 24-hours per day, seven days per week (requiring four shifts), a total of eight process operators per establishment are potentially exposed. All workers employed by catalyst service industry are estimated to be potentially exposed to hexavalent chromium.

[d] The basis of this estimate is: 14 Phillips establishments x 8 potentially-exposed workers per establishment = 112 workers; 6 UNIPOL™ establishments x 8 potentially-exposed workers per establishment = 48 workers. Total workers = 160.

[e] The number of establishments, employees, and firms in NAICS 561790 were determined by an internet search and direct contact with firms in this industry.

The catalyst service companies (NAICS 561790) identified by Shaw as large employers (20 or more employees) are:

- Cat Tech, six establishments,
- Catalyst Service, Inc., six establishments,
- JT Catalyst (a division of James Timec), three establishments,
- RSI, two establishments,
- Incat (a division of Phillips Services), two establishments,
- Gulf Coast Catalyst, (a division of Koch Specialty Plant Services), two establishments.

24.2 Process Description

One major industrial use of hexavalent chromium containing catalysts is in the polymerization of ethylene to produce polyethylene. Two different hexavalent chromium catalytic processes are used for polyethylene production, the Phillips polyolefins process and the Dow UNIPOL™ process.

Since the first commercial plant began operation in 1956, the Phillips process has been licensed to six other manufacturers in the United States and by 1980, accounted for over five billion pounds annually (Leach, 1983). The Phillips polyolefins process uses a chromium oxide-silica-alumina catalyst, which is manufactured, delivered, and loaded into the catalyst feed vessel as a trivalent chromium catalyst. This trivalent chromium catalyst is activated to the hexavalent chromium valence before use by heating the catalyst to a high temperature. The concentration of hexavalent chromium in the catalyst can vary from a few one-hundredth of a percent to several percent, but typically the concentration of total chromium is 0.5 to 1 percent. The catalyst is stored as a powder in the catalyst feed vessel under a dry atmosphere after activation and before it is flushed with nitrogen to remove entrained air. During polyethylene production, the powdered catalyst is fed into the ethylene stream before it enters a double loop reactor where ethylene is polymerized to polyethylene. The powdered hexavalent chromium catalyst is used only once in this process and leaves the process along with the polymerized polyethylene. Unlike other catalyst processes, manual catalyst removal from process vessels is not necessary because the original catalyst particle is bound together with the polymer, which contains fragmented catalyst particles throughout (Leach, 1983).

On June 24, 1994, Meridian Research, Inc. conducted a walk-through survey of a facility that used the Phillips polyolefins process to produce polyethylene. The following process description summary describes this particular facility.

This facility employed approximately 900 workers and produces several different types of plastics and various chemicals but only uses the chromium-containing catalyst in polyethylene production. Six polyethylene reactors were active at the facility.

The silica gel chromium acetate catalyst is purchased in 150-pound drums (net weight) and is initially a trivalent chromium compound that is stable in air. Before the catalyst can be used to enhance the production reactions, it must first be activated by heating the raw catalyst and allowing it to come into contact with air which produces the hexavalent chromium catalyst that must be cooled and then stored under nitrogen to prevent the catalyst from coming into contact with air, which would poison the activated catalyst. The catalyst is automatically fed into a pressure vessel on wheels (tote bin) under a nitrogen blanket. This tote bin is then moved by forklift to the reactor area, where it is hooked up to a charge line that supplies the catalyst feed system. The feed system utilizes isobutane to carry the catalyst into the reactor.

During September 3 and 4, 2003 and October 20-24, 2003, NIOSH performed an on-site health hazard evaluation and survey at the Chevron Phillips Chemical Company (CPC) Pasadena Plastics Complex located in Pasadena, Texas (NIOSH, 2004). This complex employs 750 workers for the production of specialty chemicals, including 150 operations and maintenance personnel who work at three Phillips polyolefins plants where hexavalent chromium-containing catalyst is used to produce polyethylene. This evaluation included employee interviews, air sampling, and surface wipe sampling for hexavalent chromium. The Phillips closed-loop polyolefins process is similar to the process described by Meridian. The entire activation and reaction process is closed-loop and the potential for exposures to occur only when breaking into the closed-loop system (NIOSH, 2004).

For purposes of designating required personal protective equipment (PPE), Chevron Phillips has characterized work activities as Categories A, B, and C, based on a qualitative assessment of the potential for employees to come in contact with the chromium catalyst (NIOSH, 2004).

Category A (the category of lowest anticipated contact) designates activities where it is anticipated no exposure to chromium catalyst will occur and includes touring facilities or inspecting catalyst containing equipment without opening it, and maintenance activities involving non-catalyst containing equipment. Category A activities require no special PPE beyond what is normally worn by all plant personnel: Nomex® (flame retardant) coveralls, hard hats, safety glasses or goggles, hearing protection, and safety shoes.

Category B is for activities with a "slight" potential for chromium exposure. These are activities where the catalyst should remain in the process piping, but there is a slight chance for it to be present in some fittings. Examples of Category B tasks include: inspection of open catalyst containing equipment, and opening of purged transfer hoses. Category B tasks require the use of Pyrolon® (chemical resistant, fire retardant) coveralls worn over Nomex® coveralls, gloves, and half-face air purifying respirators with High Efficiency Particulate Air (HEPA) filters.

Category C is for work activities with a "moderate" potential for exposure to chromium catalyst. Category C tasks are those in which there is a potential that the employee will come into contact with the catalyst, and decontamination procedures are required following Category C work. Category C tasks require the use of Pyrolon® disposable coveralls worn over Nomex® disposable cloth coveralls, impervious gloves, socks, rubber booth, overshoes, and half-face air purifying respirators with HEPA filters and goggles, or full-face air purifying respirator with HEPA filters.

Between January 1, 2003, and October 14, 2003, approximately 120 Category C activities were performed at the catalyst activators. This equates to approximately 13 Category C tasks per month. During the health hazard evaluation, NIOSH investigators observed employees transferring activated catalyst while charging the mud pots and transferring raw catalyst to the activator. No visible emissions of catalyst were observed during the transfer processes (NIOSH, 2004).

Exposure to hexavalent chromium during this use of chromium catalysts is minimal. There are only four non-emergency operations that have the potential to result in exposure.

1. One operation is when the raw (trivalent) catalyst is manually loaded into the catalyst activation unit. This process involves 2 operators per shift and can take between 12 and 35 hours to complete. Although the operators are loading trivalent chromium, a small amount of hexavalent material is formed during the manufacturing process.
2. The highest potential for personnel to be exposed to the activated chromium catalyst is while connecting and disconnecting transfer lines.
3. Another potential exposure to activated catalyst occurs during the task of collecting activated catalyst samples for laboratory analysis.
4. Another potential exposure occurs in the unlikely event of a batch abort, at which time catalyst is dumped from the system into a waste catalyst drum. This catalyst dumping occurs in a specially designed containment building under negative pressure and is almost entirely automated. An operator is needed to remove the waste catalyst drum from the building (Meridian Research, 1994).

In 1968, Union Carbide introduced its UNIPOL™ gas phase process for high-density polyethylene production. There are variations of the UNIPOL™ gas phase process, of which approximately 40 percent of production plants use hexavalent chromium containing catalysts and the other 60 percent of production plants use non-chromium catalysts. The hexavalent chromium catalyst used in the UNIPOL™ gas phase process is silica-based and contains 0.2 to 0.4 percent hexavalent chromium. These hexavalent chromium catalysts are produced and remain in the hexavalent chromium valence state as they are loaded into catalyst reactor vessels, and removed years later as spent catalyst. Catalyst is not added to the reaction vessel between catalyst changes but is added only once, at the time of catalyst replacement. Unlike the Phillips process, the chromium catalyst remains in the reaction vessel until the catalyst reaches the end of its service life and is removed from the reaction vessel.

Hexavalent chromium catalysts are used in dehydrogenation processes for the production of styrene from ethylbenzene and production of butadiene from 1-butene. Another dehydrogenation application, which is no longer used in the United States, is the production of methyl tertiary-butyl ether (MTBE). Although once used as a motor fuel additive to improve air quality, evidence of MTBE as a source of groundwater contamination has resulted in the drastic reduction of MTBE use (personal communication, Jim Richardson, 2003).

Hexavalent chromium catalysts are used in a hydrogenation process for the synthesis of methanol by reacting carbon monoxide with hydrogen. This process typically utilizes a zinc oxide-chromium oxide catalyst. The chromium content of the catalyst is 22 percent trivalent chromium valence and 0.1 percent hexavalent chromium. However, the dominant process used for methanol production is the ICI low-pressure process that uses a non-chromium catalyst (Kirk-Othmer, 1993). Therefore, Shaw estimates less than 25 percent of methanol plants in the United States use a chromium catalyst.

Hexavalent chromium catalysts are also used in the production of hydrogen and ammonia. Typically, iron-based catalysts are used which contain chromium, primarily as trivalent chromium, and 1 to 2 percent hexavalent chromium. This gas production process uses a water gas shift reaction, whereby carbon monoxide and water are reacted to produce carbon dioxide and hydrogen. Ammonia is produced in a water gas shift reaction of hydrogen and nitrogen.

Based on SRI, 2003 and Leach, 1983, Shaw estimates there are seven polyethylene firms and 14 establishments in the United States using the Phillips polyolefins process; and three firms and six establishments that produce polyethylene using a hexavalent chromium catalyst in the UNIPOL™ gas phase process.

The exposed employees at a polyethylene production plant that uses the Phillips polyolefins process are the operators of the process involving the hexavalent chromium catalyst vessel. Based on previous Meridian Research walk-through survey information, Shaw estimates each establishment that uses the Phillips polyolefins process has two process operators per shift who are potentially exposed to hexavalent chromium catalyst. Since these establishments operate 24 hours per day, seven days per week, a total of eight process operators per establishment are estimated to be potentially exposed to hexavalent chromium catalyst (Meridian Research, 1994).

The tasks of loading and unloading hexavalent chromium containing catalyst into and out of catalyst process reactors and holding vessels present the greatest potential for hexavalent chromium exposure among chromium catalyst users (personal communication Steve Brennom, Jim Richardson, 2003). Employees involved in loading and unloading hexavalent chromium containing catalyst are catalyst service company field technicians who load and unload catalyst, and Phillips polyolefins process operators who load catalyst into process vessels prior to activation of the catalyst.

The job category of field technician for catalyst loading and unloading operations typically includes employees who perform the following jobs. One field technician enters the catalyst vessel and handles a flexible vacuum hose that is used to vacuum and remove catalyst from the vessel. Because many catalysts are pyrophoric and may spontaneously ignite in contact with air, they are kept under a nitrogen blanket during both normal operating conditions and during the time when catalyst is unloaded and loaded. Field technicians who enter catalyst vessels regularly encounter a vessel that contains catalyst under a nitrogen blanket, and is, therefore, an oxygen deficient atmosphere. In addition, catalyst vessels are sufficiently large for a person to enter. Because these vessels are not designed for continuous human occupancy, they are considered a permit-required confined space. Field technicians are typically equipped with NIOSH-approved supplied-air line helmets which include tight-fitting full-facepiece, full-body protective suits, Nomex® or fire-retardant coveralls, with protective gloves and boots. In addition to the primary source of air provided through an air line, the entrant is provided with a 5-minute escape air bottle and a second source of emergency breathing air that is installed within the helmet (personal communication, Andrew Clark, Ken Waterhouse, 2003).

In addition to the field technician who enters the catalyst vessel, a second field technician is stationed at the entrance to the vessel and serves as the confined space attendant. The technician stationed at the entrance to the vessel is equipped with a respirator, fire-retardant coveralls, protective gloves, and boots. A third field technician operates the support equipment, including the breathing air supply system, the vacuum truck or vacuum system that removes the catalyst from the vessel, the dust collector that removes dust from the vacuum system exhaust catalyst screening system, and if used, the catalyst screening unit. Other support personnel who are not considered exposed employees from a hexavalent chromium exposure standpoint are the job site supervisor and heavy equipment operators including crane or forklift operators (personal communication, Andrew Clark, Ken Waterhouse, 2003).

As indicated earlier, over 90 percent of catalysts (including hexavalent chromium catalyst) are loaded and unloaded by catalyst service companies. Therefore, less than 10 percent of catalyst plants utilize their own employees to load and unload catalyst into and out of catalyst process vessels. Using 10 percent as a conservative estimate, no more than 10 percent of the employees listed in Table 24-1 under NAICS Codes 325110, 325120, 325211, and 325199 handle hexavalent chromium catalyst. Therefore, an estimated 10 percent of the 1,304 affected employees in these NAICS codes (or 130 employees) handle hexavalent chromium catalyst and may encounter hexavalent chromium exposures similar to workers employed by catalyst service companies (NAICS 561790). According to catalyst service company personnel, hexavalent chromium-containing catalysts are infrequently handled and catalyst handling projects were estimated to occur less than 30 days per year (personal communication, Andrew Clark, Ken Waterhouse, 2003).

Because hexavalent chromium catalysts are contained within fully-enclosed process vessels, the potential for production plant employee exposure to hexavalent chromium is minimal. Therefore, process operators at production facilities that use hexavalent chromium catalyst (other than the Phillips polyolefins process operators who handle the chromium catalysts on a regular basis) and utilize catalyst service companies for catalyst handling are estimated to have negligible exposure.

The estimated number of workers exposed to chromium in each job category, are presented in Table 24-2. These estimates are based on information from the Meridian site walk (Meridian Research, 1994) and personal communication with representatives in the catalyst service industry (Steve Brennom, Andrew Clark, Ken Waterhouse and Paul Caskey, 2003).

Table 24-2. Number of Employees Exposed to Hexavalent Chromium by Job Category for Chromium Catalyst Users

Job Category	Number of Employees in Large Facilities[a]	Number of Employees in Small Facilities[b]	Total Number of Employees
Process Operators, Phillips polyethylene plants	112 [c]	0	112
Process Operator, all catalyst plants except Phillips polyethylene plants	130	0	130
Field Technicians, Catalyst Service Companies	640	60	700
Total	882	60	942

a Estimate of number of employees in large catalyst service companies is derived from personal communications with representatives in the catalyst service industry.

b Number of employees per job category in small facilities is based on a model small facility whose average employment exposed to hexavalent chromium is fifteen workers per facility.

c Estimate of number of employees in large Phillips polyethylene plants is derived from information in Meridian Site Visit (Meridian Research, 1994). The basis of this estimate is: 14 Phillips establishments x 8 potentially-exposed workers per establishment = 112 workers.

24.3 Exposure Profile

No NIOSH or site visit hexavalent chromium exposure data is available for catalyst service company field technicians who perform catalyst loading and unloading at catalyst user facilities. In addition, no exposure data is available from the Occupational Safety and Health Administration (OSHA) Integrated Management Information System (IMIS) database for this industry.

As described earlier, during the walk-through survey conducted at a facility that used the Phillips polyolefins process to produce polyethylene, Meridian Research obtained data on process operator exposure monitoring performed by the facility. Individual data points are not available, however; a statistical analysis of the 11 personal time-weighted average (TWA) samples for hexavalent chromium taken by this facility between 1993 and 1994 revealed that the geometric mean was 0.327 $\mu g/m^3$ and the geometric standard deviation was 1.867. This facility used NIOSH method 7600 for its collection and analysis of hexavalent chromium samples (Meridian Research, 1994). Utilizing Equation 13.24 from "Statistical Methods for Environmental Pollution Monitoring," (Gilbert, 1987), Shaw calculated the distribution of exposure data points for process operators at Phillips polymerization plants, presented in Table 24-3a, for inclusion in the exposure profile (Table 24-4) (Gilbert, 1987).

Table 24-3a. Full-Shift Hexavalent Chromium Calculated Monitoring Data from a Site Visit to a Phillips Polyolefin Production Facility (Merician Research, 1994)

Job Category	Hexavalent Chromium Exposure Range [a] ($\mu g/m^3$)
Process Operators, Phillips polyethylene plants	Below LOD
	Below LOD
	0.25 to 0.5
	0.25 to 0.5
	0.5 to 1.0
	0.5 to 1.0
	0.5 to 1.0
	1.0 to 5.0
	1.0 to 5.0
	5.0 to 10.0
	5.0 to 10.0

[a] Individual data points are not available, however; a statistical analysis of the 11 personal time-weighted average (TWA) samples for hexavalent chromium taken by this facility between 1993 and 1994 revealed that the geometric mean was 0.327 $\mu g/m^3$ and the geometric standard deviation was 1.867. The distribution of exposure data was calculated from this statistical information.

The NIOSH health hazard evaluation performed at the Chevron Phillips Chemical Company (CPC) Pasadena Plastics Complex included full-shift personal exposure sampling on 32 operations personnel, two maintenance personnel, and one laboratory technician. Operations personnel work 12-hours shifts and maintenance personnel work 8-hour shifts. Samples were collected and analyzed for hexavalent chromium according to NIOSH Method 7605 (draft). As of September, 2003, there were 91 operators and 65 maintenance personnel assigned to work at the three Phillips closed-loop (polyolefin) polyethylene plants. Table 24-3b presents the full-shift hexavalent chromium exposure data collected by NIOSH.

In the absence of exposure data for the job category of catalyst service field technician, Shaw estimated that exposures of the catalyst screener job category in the catalyst manufacturing industry to be similar to the catalyst service field technician job category in the catalyst user industry. Exposure data for the job category of catalyst screener from the catalyst manufacturing industry will be used in the exposure profile to represent:

1) the catalyst service field technician's exposure, and
2) exposure of process operators at catalyst plants except Phillips polyethylene plants who perform catalyst loading and unloading tasks, because both jobs involve handling and screening catalyst.

Table 24-3b. Full-Shift Hexavalent Chromium Monitoring Data from a NIOSH Health Hazard Evaluation at Polyethylene Production Plants, Chevron Phillips Chemical Company, Pasadena Plastics Complex (NIOSH, 2004)

Job Category	Hexavalent Chromium Exposure [a] ($\mu g/m^3$)
Process Operators, Phillips polyethylene plants	ND [a]
	ND
	ND
	ND
	ND
	ND
	ND
	ND
	ND
	ND
	ND
	ND
	ND
	ND
	Trace [a]
	Trace
	Trace
	Trace
	Trace
	Trace
	Trace
	Trace
	Trace
	Trace
	0.09
	0.09
	0.09
	0.09
	0.10
	0.12
	0.39

[a] The average blank concentration of 0.13 µg/sample was subtracted from the sample results before calculating the 10-hour time weighted average (TWA). Where the 10-hour TWA was less than $0.03 \mu g/m^3$ the results were reported as ND (non-detected). Results between $0.03 \mu g/m^3$ and $0.08 \mu g/m^3$ were reported as "Trace".

Exposures to hexavalent chromium are estimated to be similar because catalyst is handled and screened by the catalyst service field technician during catalyst removal, in a fashion similar to the catalyst screening process employed during manufacturing. In the catalyst manufacturing industry, hexavalent chromium containing catalyst that has been manufactured and formed into a shape is passed through screening equipment that sorts the catalyst by size. The screening process occurs near the end of the catalyst manufacturing process, prior to loading the catalyst into finished product containers.

Table 24-3c presents the full-shift TWA exposure for catalyst screening operations at catalyst production facilities. The median exposure for the job category of catalyst screening operator calculated from the data in Table 24-3c is 0.70μg/m³. These exposure data are used in Table 24-4 to represent the distribution of hexavalent chromium exposure of catalyst service company field technicians and process operators at chemical production plants who perform hexavalent chromium catalyst handling tasks.

Table 24-3c. Full-Shift Hexavalent Chromium Monitoring Data at Catalyst Production Facilities from Site Visits to Companies N and R [a]

Site Visit	Job Category	Hexavalent Chromium Exposure (μg/m³)[b]
Company N [c]	Screening Operator	0.15 [e]
	Screening Operator	0.47 [f]
	Screening Operator	0.48
	Screening Operator	6.8 [g]
Company R [d]	Screening Operator	<0.93
	Screening Operator	<1.1

a – All samples reported are personal, full-shift TWA (Time-weighted average).
b - μg/m³ = Micrograms per cubic meter.
c – Data collected by IT Corporation during the 1997 site visit to a hexavalent chromium production facility.
d - Data collected by Company R (hexavalent chromium catalyst production facility) during 1996.
e – This screening operator processed a non-chromium catalyst, but was working in the area where a hexavalent chromium catalyst was being screened.
f - This screening operator drove a forklift in the screening area and performed other material handling operations.
g – The screening operator processed a hexavalent chromium catalyst.

Table 24-4 presents full-shift worker exposures for hexavalent chromium in industries hexavalent chromium containing catalysts. In Table 24-4, each of the two facilities sampled is weighted equally. The exposure profile in Table 24-5 applies the percentage of hexavalent chromium results in each range for job categories in Table 24-4 to the population of production workers potentially exposed to hexavalent chromium.

Table 24-4. Distribution of Full-Shift Personal Exposures (8-hour TWA) for Hexavalent Chromium in Catalyst Using Industries, Based on Site Visit Data from Catalyst Users and Catalyst Producers

Job Category	Total No. of Data Points	Distribution ($\mu g/m^3$)[a]							
		Below LOD[b]	LOD to <0.25	0.25 to <0.5	≥0.5 to <1.0	≥1.0 to <5.0	≥5.0 to <10.0	≥10.0 to <20.0	≥20.0
Process Operators, Phillips polyethylene plants	42	16 (34%)	16 (25%)	3 (10%)	3 (13%)	2 (9%)	2 (9%)	0 (0%)	0 (0%)
Process Operators, all catalyst plants except Phillips polyethylene plants	6	0 (0%)	1 (16.6%)	2 (33%)	1 (16.6%)	1 (16.6%)	1 (16.6%)	0 (0%)	0 (0%)
Field Technician	6	0 (0%)	1 (16.6%)	2 (33%)	1 (16.6%)	1 (16.6%)	1 (16.6%)	0 (0%)	0 (0%)

[a]$\mu g/m^3$ = Micrograms per cubic meter.
[b]LOD = Limit of detection.

Table 24-5. Personal Exposure Profile in Catalyst Using Industries (Full-Shift TWA), Based on Site Visit Occupational Data[a]

Job Category	Total No. of Workers	Distribution ($\mu g/m^3$)[b]							
		Below LOD[b]	LOD to <0.25	0.25 to <0.5	≥0.5 to <1.0	≥1.0 to <5.0	≥5.0 to <10.0	≥10.0 to <20.0	≥20.0
Process Operators, Phillips polyethylene plants	112	38 (34%)	28 (25%)	11 (10%)	15 (13%)	10 (9%)	10 (9%)	0 (0%)	0 (0%)
Process Operators, all catalyst plants except Phillips polyethylene plants	130	0 (0%)	22 (16.6%)	43 (33%)	22 (16.6%)	22 (16.6%)	22 (16.6%)	0 (0%)	0 (0%)
Field Technician	707	0 (0%)	119 (16.6%)	231 (33%)	119 (16.6%)	119 (16.6%)	119 (16.6%)	0 (0%)	0 (0%)
Total	949	38 (4%)	169 (17%)	285 (31%)	156 (16%)	151 (16%)	151 (16%)	0 (0%)	0 (0%)

[a]Values may be affected by rounding.
[b]$\mu g/m^3$ = Micrograms per cubic meter.
[c]LOD = Limit of detection.

24.4 Technological Feasibility

24.4.1 Baseline Controls

Information regarding baseline controls for process operators at Phillips polyethylene plants was obtained during the facility walk through survey conducted by Meridian Research at a polyethylene production facility (Meridian Research, 1994). Information regarding baseline controls for catalyst service company field technicians was obtained through personal communication with occupational health and safety professionals and other personnel at catalyst service companies. It is estimated that all facilities that use or handle hexavalent chromium containing catalyst have similar controls and work practices.

Process Operator, Phillips Polyethylene Plants

As manufactured and received in 150-pound drums, the chromium catalyst for the Phillips polyethylene process is a trivalent chromium catalyst, with only a minor amount of hexavalent chromium as a by-product from the manufacturing process. The process operators manually pour the catalyst from the drums into the process vessel that are subsequently closed and sealed before the catalyst is activated from trivalent chromium to a hexavalent chromium valence state. No information is currently available regarding any engineering controls, specific work practices, or personal protective equipment used during this catalyst-loading task

An engineering control is in place to control potential exposure in the unlikely event of a batch abort, at which time the catalyst, which had been activated to hexavalent chromium, is dumped from the system into a waste catalyst drum. This catalyst dumping occurs in a specially designed containment building under negative pressure and is almost entirely automated. An operator is then needed to remove the waste catalyst drum from the building (Meridian Research, 1994). Work practices or PPE used by the operator for this task are unknown.

Process Operators, All Catalyst-Using Plants Except Phillips Polyethylene Plants

No specific information is available for those facilities that do not use the services of catalyst service companies, but instead use their own operators to load and unload catalyst. However, the tasks performed by process operators are the same as those performed by field technicians employed by catalyst service companies. Shaw estimates the engineering controls, work practices, and PPE used by these employees are the same as those used by catalyst service company field technicians.

Field Technicians, Catalyst Service Companies

Field technicians who enter catalyst vessels regularly encounter a vessel that contains catalyst under a nitrogen blanket, and is therefore, an oxygen deficient atmosphere. Because a nitrogen blanket is maintained in the catalyst vessel, use of mechanical ventilation to control airborne catalyst dust is not feasible. Therefore, PPE and confined space safety work practices are used to control employee exposure to air contaminants. For working in catalyst vessels that have an oxygen deficient atmosphere, these technicians are equipped with NIOSH-approved supplied-air line helmets, which include tight-fitting full-facepiece, full-body protective suits, Nomex® or fire-retardant coveralls, with protective gloves and boots. In addition to the primary source of air provided through an air line, the entrant is provided with a 5-minute escape air bottle and a second source of emergency breathing air that is installed within the helmet. If the catalyst vessel is not kept under nitrogen blanket during catalyst removal/loading operations, the technician who enters the vessel may wear a full-face air-purifying respirator, or dust mask, depending on the potential air contaminants anticipated in the catalyst vessel (personal communication, Andrew Clark, Ken Waterhouse, 2003).

In addition to the field technician who enters the catalyst vessel, a second field technician, who is equipped with respiratory protection and other PPE described previously, is stationed at the entrance to the vessel and serves as the confined space attendant. A third field technician operates the support equipment, including the breathing air supply system, the vacuum truck or vacuum system that removes the catalyst from the vessel, the dust collector that removes dust from the vacuum system exhaust catalyst screening system, and if used, the catalyst screening unit.

24.4.2 Additional Controls

24.4.2.1 Additional Controls to Achieve a 20 $\mu g/m^3$ 8-Hour TWA Alternative PEL

Based on current full-shift hexavalent chromium exposures, no additional controls will be required to achieve 8-hour TWA exposures of less than 20$\mu g/m^3$ for any of the three job categories of workers involved in catalyst handling. These job categories are Process Operator - Phillips Polyethylene Plants, Process Operators - All Catalyst-Using Plants Except Phillips Polyethylene Plants, and Field Technicians - Catalyst Service Companies.

24.4.2.2 Additional Controls to Achieve a 10 $\mu g/m^3$ 8-Hour TWA Alternative PEL

Based on current full-shift hexavalent chromium exposures, no additional controls will be required to achieve 8-hour TWA exposures of less than 10$\mu g/m^3$ for any of the three job categories involved in catalyst handling. These job categories are Process Operator - Phillips Polyethylene Plants, Process Operators - All Catalyst-Using Plants Except Phillips Polyethylene Plants, and Field Technicians - Catalyst Service Companies.

24.4.2.3 Additional Controls to Achieve a 5 $\mu g/m^3$ 8-Hour TWA Alternative PEL

Based on current full-shift hexavalent chromium exposures, no additional controls will be required to achieve 8-hour TWA exposures of less than 5$\mu g/m^3$ for any of the three job categories involved in catalyst handling. These job categories are Process Operator - Phillips Polyethylene Plants, Process Operators - All Catalyst-Using Plants Except Phillips Polyethylene Plants, and Field Technicians - Catalyst Service Companies.

24.4.2.4 Additional Controls to Achieve a 1 $\mu g/m^3$ 8-hour TWA Alternative PEL

Based on current full-shift hexavalent chromium exposures, no additional controls will be required to achieve 8-hour TWA exposures of less than 1$\mu g/m^3$ for any of the three job categories of workers described previously.

24.4.2.5 Additional Controls to Achieve a 0.5 $\mu g/m^3$ 8-Hour TWA Alternative PEL

Based on current full-shift hexavalent chromium exposures, additional controls will be required for the job categories of Process Operators - All Catalyst-Using Plants Except Phillips Polyethylene Plants, and Field Technicians - Catalyst Service Companies to achieve 8-hour TWA exposures of less than 0.5$\mu g/m^3$.

Shaw estimates that exposures result from confined space entry into catalyst vessels for the job categories of Process Operators - All Catalyst-Using Plants Except Phillips Polyethylene Plants, and Field Technicians - Catalyst Service Companies. As presented previously, engineering controls such as local exhaust ventilation for entry into catalyst vessels is not feasible. Therefore respiratory protection will be necessary. However, personnel who enter catalyst vessels are usually equipped with some form of respiratory protection for protection from oxygen deficiency or other air contaminants. Therefore, use of respiratory protection should not be considered as additional PPE beyond what is currently used for these job categories.

24.4.2.6 Additional Controls to Achieve a 0.25 $\mu g/m^3$ 8-Hour TWA Alternative PEL

Based on current full-shift hexavalent chromium exposures, the additional control of respiratory protection as presented previously, will be adequate to achieve 8-hour TWA exposures of less than $0.25\mu g/m^3$ for two job categories of workers: Process Operators - All Catalyst-Using Plants Except Phillips Polyethylene Plants, and Field Technicians - Catalyst Service Companies.

Based on current full-shift hexavalent chromium exposures, additional controls will be required to achieve 8-hour TWA exposures of less than $0.25\mu g/m^3$ for workers in job category of Process Operator - Phillips Polyethylene Plants.

For the job category of Process Operator - Phillips Polyethylene Plants, the engineering control of equipping the catalyst vessel with exhaust ventilation will achieve the alternative PEL of $0.25\mu g/m^3$. This exhaust ventilation system should be connected directly to the catalyst vessel so that the catalyst vessel is under negative pressure, resulting in air flow into the open hatch where the catalyst is loaded. Similar controls can be found as baseline controls at a catalyst raw material mixing tank at company R, and similar mixing tanks at chromate copper arsenate (CCA) production facilities where solid chromic acid flake is poured into a mixing tank. These controls were found to achieve hexavalent chromium exposures ranging from 1.7 to $12\mu g/m^3$. However, because the chromic acid at these other facilities contains 100 percent hexavalent chromium, as compared with the catalyst used in the Phillips process that contains trace amounts of hexavalent chromium, this engineering control is estimated to reduce hexavalent chromium exposures by at least an order of magnitude. As presented in the process description subsection, the catalyst particles are encapsulated into the polyethylene product, resulting in catalyst removal from the feed vessel by the process. Therefore, manual catalyst removal from the vessel is not necessary.

24.4.3 Substitutes for Chromate-Containing Catalysts

As presented in subsection 24.2, the UNIPOL™ gas phase process for high-density polyethylene production is an alternative manufacturing process to the Phillips polyolefins process. There are variations of the UNIPOL™ gas phase process, of which approximately 40 percent of production plants use hexavalent chromium containing catalysts and the other 60 percent of production plants use non-chromium catalysts. Because the UNIPOL™ gas phase process can produce polyethylene using non-chromium catalysts, this process can be substituted for the chromium-containing Phillips polyolefins and UNIPOL™ gas phase catalyst processes.

No information is available regarding substitutes for other hexavalent chromium containing catalyst processes.

24.5 References

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